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Revisiting the open-framework zinc hexacyanoferrate: The role of ternary electrolyte and sodium-ion intercalation mechanism

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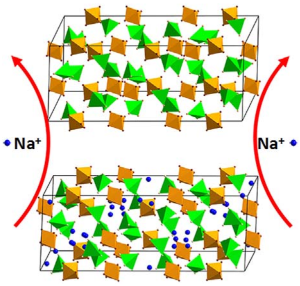
HIGHLIGHTS

- A sodium-ion battery with a high voltage output of 1.6 V is achieved.
- Ternary electrolyte delivers high ionic conductivity and low activation energy.
- Sodium-ion intercalation mechanism of zinc hexacyanoferrate is revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

Non-flammable rechargeable aqueous sodium-ion batteries (RASB) made from natural abundant resources offer promising opportunities in large-scale energy storage, yet the low energy density as well as low voltage output and the limited cycle life hinder their practical applications. Here, we develop a high-voltage RASB based on rhombohedral zinc hexacyanoferrate as cathode materials, carbon-coated $NaTi_2(PO_4)_3$ as anode materials and ternary $NaClO_4$-H_2O-polyethylene glycol (Na-H_2O-PEG) as electrolyte to overcome these drawbacks. Such an RASB can deliver a high voltage output of 1.6 V with a specific energy density of 59 Wh kg^{-1} based on the total mass of active electrode materials. In addition, it possesses an excellent rate capability as an ultra-capacitor (2.7 kW kg^{-1}). The capacity retention more than 91% is obtained after 100 cycles. Finally, a reversible phase transformation between rhombohedral $Zn_3[Fe(CN)_6]_2$ and rhombohedral $Na_2Zn_3[Fe(CN)_6]_2$ that are accompanied by the insertion/extraction of sodium ion in zinc hexacyanoferrate is unveiled.

1. Introduction

To meet the growing requirements for the sustainable and renewable energy such as solar and wind power, great efforts are made to develop economic and safe techniques for large-scale energy storage around the world [1–3]. Rechargeable aqueous metal-ion batteries (RAMB) are considered as one of the most promising techniques for electrochemical energy storage on a large scale, due to their several advantages such as low-cost, good safety, high-rate capability and environmentally friendliness [4–7]. Up to now, a variety of RAMB have been explored in the literature and they can be divided into different categories on a basis of metal-ion (Li^+, Na^+, K^+, Zn^{2+}, Mg^{2+}, Ca^{2+} and Al^{3+}) as electrochemical shuttles. In particular, RAMB with alkali cations as electrochemical shuttles have been extensively studied.

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Among them, rechargeable aqueous sodium-ion batteries (RASB) are most competitive for grid-scale energy storage owning to the higher natural abundance of sodium relative to lithium and potassium [8–17].

As Na^+ (102 p.m.) has larger radii than Li^+ (76 p.m.), it is rather difficult to find suitable compounds for the reversible (de)intercalation of sodium ion in aqueous media. Accordingly, the known RASB are limited, and most of them suffer the problem of low energy density due to the low voltage output (< 1.2 V) [2,18]. Yamaki et al. [19] have studied the electrochemical behavior of $NaTi_2(PO_4)_3$ in aqueous Na_2SO_4. Its redox potential is −0.6 V *vs.* standard hydrogen electrode (SHE), implying that $NaTi_2(PO_4)_3$ is a good anode candidate for RASB. Additionally, layered-structured $Na_2V_6O_{16}$ and tunnel-type $Na_{0.44}Mn_xTi_{1\text{-}x}O_2$ have been also studied as anode materials for RASB [20,21]. But they deliver a lower specific capacity (ca. 40 mAh g^{-1}) and a higher redox potential (ca. −0.4 *vs.* SHE), when compared to $NaTi_2(PO_4)_3$. Choi's group has reported that disodium naphthalenediimide (SNDI) with a well-defined redox plateau at −0.14 V *vs.* SHE exhibits poor ion-conductivity [22]. In terms of cathode materials, many studies focus on layered-structured A_xMnO_2, tunnel-type $Na_{0.44}MnO_2$ and open framework metal hexacyanoferrates (MeHCF) [10,18,23–28]. In general, metal hexacyanoferrates have a formula of $A_nP_xQ_yFe(CN)_6$ ($0 \le n \le 2$, $x + y = 1$), while A is the alkali metals, and P & Q are the transition metals. Depending on transition metals P and Q, MeHCF can have a cubic or rhombohedral structure that enables the fast diffusion of alkali cations. Compared to other cathode materials, MeHCF always have higher working voltage, implying that they can act as promising cathode candidates for RASB. Their working voltages (*vs.* SHE) follow the order: ZnHCF (1.1 V) > NiZnHCF (0.76 V), CuHCF (0.85 V), NiHCF (0.59 V), CoHCF (0.57 V), CuCoHCF (0.9 V). Among them, ZnHCF exhibits a rhombohedral structure with a three-dimensional framework made up of FeC_6 octahedra and ZnN_4 tetrahedra linked together by the C-N groups. Our previous studies have shown that ZnHCF can act as a host for Na^+ as well as Li^+, K^+ and Zn^{2+}. However, ZnHCF undergoes rapid dissolution in common aqueous electrolytes, which hinders its practical application in RAMB.

In this work, rhombohedral ZnHCF microcubes with a uniform size are prepared by a modified precipitation reaction method. Their electrochemical properties in ternary $NaClO_4$-H_2O-polyethylene glycol (Na-H_2O-PEG) electrolyte have been also explored. By combining it with carbon-coated $NaTi_2(PO_4)_3$ as a anode material, an RASB based on Na-H_2O-PEG electrolyte with a high voltage output of 1.6 V is validated. Meantime, such an RASB exhibits a high power density as an ultracapacitor and a good cycle life. Finally, the sodium-ion intercalation chemistry in ZnHCF is revealed by using multiple characterization means.

2. Experimental

Material syntheses: Zinc hexacyanoferrate was synthesized using coprecipitation method from our previous literature [3]. To tune the particles morphology of ZnHCF, the samples were prepared as follows [29]. 5 mL of 0.075 M $ZnSO_4$, 20 mL of 0.2 M $Na_2C_2O_4$ and 10 mL of 0.05 M $K_3[Fe(CN)_6]$ aqueous solutions were sequentially added into 60 mL de-ionized water under vigorous stirring at room temperature. Then, 2.0 M HNO_3 was slowly added by a transfer pipet until the slurry was formed. Finally, the slurry was centrifuged at 8000 r.p.m. for 45 min and washed with de-ionized water and ethanol several times before dried at 100 °C overnight. $NaTi_2(PO_4)_3$ was prepared by solid-state reaction method [2]. The high purity TiO_2 (up to 99.9%), Na_2CO_3 and $NH_4H_2PO_4$ with a mass ratio of 4:1:6 were mixed with ethanol and paste was ball-milled at 400 r.p.m. for 10 h. After ball milling, the paste was dried at 80 °C and ground to powder. Then the powder was subsequently calcined for 5 h at 300 °C and for 12 h at 900 °C under air. The obtained white $NaTi_2(PO_4)_3$ solids were homogenized for further use. For the carbon-coated $NaTi_2(PO_4)_3$, $NaTi_2(PO_4)_3$ and glucose (mass ratio 5:4) were mixed with an appropriate amount of ethanol and the mixture was ball-milled for 4 h. The solids were obtained by evaporating the ethanol at 80 °C. After calcined at 800 °C for 5 h in a mixture gas (C_2H_4/Ar, 5/95), the solids became black, implying that $NaTi_2(PO_4)_3$ were coated by carbon. The Na-H_2O-PEG electrolyte was made up of $NaClO_4$, H_2O and polyethylene glycol-400 (Sinopharm Group Co. Ltd) with a mass ratio of 1.13:1.00:1.46.

Materials characterization: X-ray diffraction patterns of the samples and the electrodes at different charging/discharging states were performed on an AXS D8 Advance diffractometer (Cu *K*α radiation, λ = 1.5406 A; receiving slit, 0.2 mm; scintillation counter, 40 mA; 40 kV) from Bruker Inc. The morphology of ZnHCF particles was observed by a Hitachi S-4800 field emission SEM at an accelerating voltage of 7 kV. X-ray photoelectron spectra (XPS) of the electrodes at different charging/discharging states were collected by a Shimadzu/Kratos AXIS Ultra XPS spectrometer. The binding energy of the F1s peak (688.2 eV) from polyvinylidene fluoride was selected as a reference for calibration.

Electrochemical measurements: Electrochemical properties of positive/negative electrodes were measured using either a two-electrode or a three-electrode cell setup. For three-electrode set-up, an Ag/AgCl electrode and Pt gauze were employed as reference and counter electrodes, respectively. Active electrode materials, super P and polyvinylidene fluoride (PVDF) with a weight ratio of 75:15:10 were mixed in N-methyl-2-pyrrolidinone to make slurries. Then the slurries were coated on Ti grid and dried at 80 °C for 16 h. Discs of Ti grid with a diameter of 1.3 cm is cut for electrochemical measurements. The loading mass on each disc is kept between 4 and 6 mg.

3. Results and discussion

3.1. Structure of rhombohedral zinc hexacyanoferrate

ZnHCF can be easily prepared by the precipitation reaction of Zn^{2+} and $[Fe(CN)_6]^{3-}$ in our previous studies. But such a precipitation reaction is very fast, and the growth of ZnHCF nanocrystals can not be controlled, which results in irregular shapes of ZnHCF. It is well-known that controllable growth of nanocrystals is very important for the uniform morphology and size. A modified precipitation reaction is proposed to prepare highly ordered ZnHCF microcubes. Firstly, $ZnSO_4$, $Na_2C_2O_4$ and $K_3[Fe(CN)_6]$ are added into de-ionized water. In this solution, dissociated oxalate ions from $Na_2C_2O_4$ can form complexes with Zn^{2+}, and they are also unreactive with $[Fe(CN)_6]^{3-}$. Then, the controllable release of Zn^{2+} from complexes can be tuned by adding HNO_3 into solution, which leads to the slow growth of ZnHCF crystals. Finally, the yellow ZnHCF precipitates consisted of microcubes with a uniform size are obtained. X-ray diffraction (XRD) technique is used to identify the crystal structure of as-prepared ZnHCF. Fig. 1a shows its corresponding XRD patterns along with the Rietveld refinement. As shown, all the peaks are well-indexed to $Zn_3[Fe(CN)_6]_2$ (JCPDS # 38–0688) without any impurities, which can be ascribed to the rhombohedral structure (space group *R-3c*). In such a structure, FeC_6 octahedra and ZnN_4 tetrahedron are linked together by C-N ligands to form a three-dimensional framework that contains a lot of interstitial sites (see Fig. 1b). Through Rietveld refinement, the lattice parameters *a*, *b*, *c* are found to be 12.604, 12.604 and 32.971 Å, respectively, which are in good agreement with the literature [30]. Other calculated structural parameters including bond distances, bond angles and fractional coordinates are summarized in Supplementary Tables 1 and 2 The morphologies of ZnHCF are further characterized by scanning electron microscopy (SEM). Highly ordered ZnHCF cubes with a uniform size of ca. 2 μm are found. Such cubes look like “toy bricks” that can be assembled into different shapes.

3.2. Role of ternary electrolyte

Polyethylene glycol (PEG) with a general formula of HO-